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Recent advances on microbial activity of metal complexes: A short review

Md Saddam Hossain[1], Md Abdul Mannan[2], Md Kudrat-E-Zahan[3*]
[1] Department of Chemistry, Begum Rokeya University, Rangpur, Bangladesh
[2-3] Department of Chemistry, Rajshahi University, Rajshahi, Bangladesh

Abstract
Metal ions play many critical functions in humans. Deficiency of some metal ions can lead to disease like pernicious anemia resulting from iron deficiency, growth retardation arising from insufficient dietary zinc, and heart disease in infants owing to copper deficiency. Cancer is one of the most fatal diseases, with which millions of people die in unbearable pain every year all over the world. Almost everybody shows extreme fear of cancers and mostly turn pale once mentioning cancers. At the same time, antibiotic resistance has been growing at an alarming rate and consequently the activity of antibiotics against Gram-negative and Gram-positive bacteria has dropped dramatically day by day. In this sense there is a strong need to synthesis new substances that not only have good spectrum of activity, but having new mechanisms of action. Inorganic compounds particularly metal complexes have played an important role in the development of new metal based drugs. A significantly rising interest in the design of metal complexes as drugs and diagnostic agents is currently observed in the area of scientific inquiry, specifically termed medicinal inorganic chemistry. In this review our main focused on research proceed by Md. Kudrat-E-Zahan and *et al.* over the past few years.

Keywords: Metal complexes, Schiff base, mixed ligand complexes, antibacterial activity, cytotoxicity etc

Introduction
Metal complexes appear to provide a rich platform for the design of novel chemotherapeutic drugs. We can choose the metal itself and its oxidation state, the numbers and types of coordinated ligands and the coordination geometry of the complexes. The ligands can not only control the reactivity of the metal, but also play critical role in determining the nature of secondary coordination sphere interactions involves in the recognition of biological target sites such as DNA, enzymes and protein receptors. Also the ligands themselves can sometimes undergo biologically-important redox reactions or other modifications (e.g hydrolysis) *in vivo* mediated by the metal. These variables provide enormous potential diversity for the design of metallo-drugs [1-3]. The introduction of metal ions or metal ion binding components into a biological system for the treatment of diseases is one of the main subdivisions in the field of bioinorganic chemistry [4]. A characteristic of metals is that they easily lose electrons to form positively charged ions which tend to be soluble in biological fluids. It is in this cationic form that metals play their role in biology. Metal ions are electron deficient, whereas most biological molecules such as proteins and DNA are electron rich. The attraction of these opposing charges leads to a general tendency for metal ions to bind and interact with biological molecules [5-7]. This same principle applies to the affinity of metal ions for many small molecules and ions crucial to life, such as oxygen. Given this wide scope for the interaction of metals in biology, it is not surprising that natural evolution has incorporated many metals into essential biological functions. Metals perform a wide variety of tasks such as carrying oxygen throughout the body and shuttling electrons. Hemoglobin, an iron-containing protein that binds to oxygen by which it carries this vital molecule to body Tissues. Similarly, calcium-containing minerals are the basis of bones, the structural framework of the human body. Metals such as copper, zinc, iron and manganese are incorporated into catalytic proteins, the metalloenzymes, which facilitate a multitude of chemical reactions needed for life. Metal complexes are already in clinical use, and encourage further studies for new metallo drugs such as metal mediated antibiotics, antibacterials, antivirals, antiparasitics, anti-HIV [8, 9], anti-diabetes, radio-sensitizing agents and anticancer compounds [9-13]. Transition metal complexes offer two distinct advantages as DNA-binding agents [14, 15].

Metal Complexes as Biologically Active
Antibiotics are substances which, even at low concentrations, inhibit the growth and reproduction of bacteria and fungi. The treatment of infectious diseases would be inconceivable today without antibiotics. M.S. Islam and *et al* [16] were synthesized Pd(II), Pt(IV), Rh(III) and Fe(III) mixed ligand complexes with diphenic acid and heterocyclic amines.The ligand and metal complexes have been screed for antibacterial activities aganist various gram positive and gram negative bacterial species. M. Akter Farooque and *et al.* [17]. M. Alim-Al-Bari and *et al* [18] were synthesized four ferrocene derivatives and their metal complexes. The ligands and metal complexes were also screened against various bacterial species also showed cytotoxicity against brine shrimp. The antimicrobial and cytotoxic activities of two new chromium based coordination complexes [Cr (Pht)$_2$ (Cystine)$_2$] indicated C_1 and [Cr(Suc)$_2$(Phenylamine)$_2$] indicated C_2, were investigated against Gram-positive and Gram-negative bacteria, fungi, and brine shrimp nauplii by M. Abdul Alim-Al-Bari and *et al* [19]. Mixed ligand metal complexes of Mn

(II), Co (II), Ni (II), Cu (II) and Zn (II) with ferrocene dicarboxylates have been synthesized and characterized by M. Abdul Alim-Al-Bari and *et al.* [20]. Antimicrobial activity of the complexes have been examined against eight Gram positive and Gram negative pathogenic bacteria and four pathogenic fungi by disc diffusion method and compared with that of standard antibiotics (Kanamycin for antibacterial activity and Fluconazole for antifungal activity). These complexes have been found to be moderate to strong antimicrobial activity against the tested microbes. Brine shrimp eggs were hatched in artificial sea water and exposed to the complexes. The mixed ligand complexes of Co(II) with amino acids and heterocyclic amines (fig-1) have been synthesized and characterized by Md. Kudrat-E-Zahan and *et al.* [21]. The antibceteril activity of the ligand and metal complexes have been screened aganist various gram positive and gram negative bacterial species.

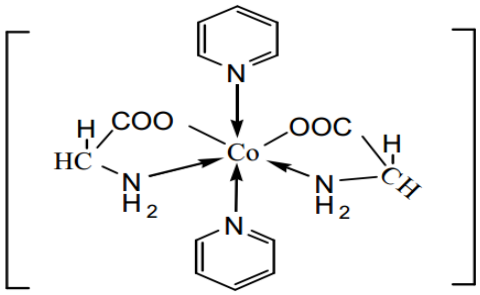

Fig 1: Structure of the complex [Co (II)$(Gly)_2$ $(Py)_2$]

The synthesis of Cr(III) / Fe(III) metal complexes with amino acids and heterocyclic amines has been carried out by Md. Kudrat-E-Zahan and *et al.* [22]. Antibacterial activity of the complexes has been examined against six (gram positive and gram negative) pathogenic bacteria by disc diffusion method and compared with that of standard antibiotic (Kanamycin). The Fe(III) complexes (fig-2) was found to have strong antibacterial activity against the tested bacteria than Cr(III) complex (fig-3).

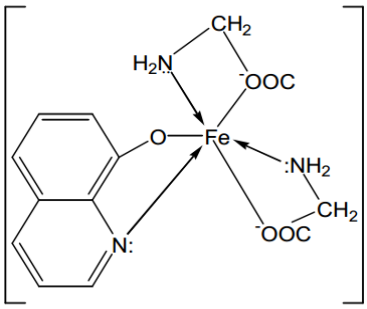

Fig 2: Structure of complex [Fe (III) (Gly)2(8-HQ)]

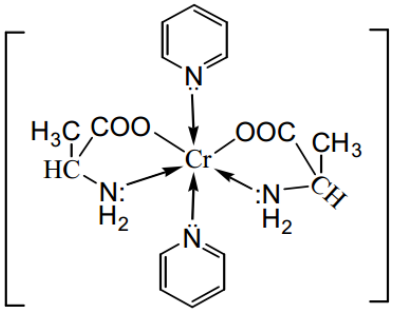

Fig 3: Structure of complex [Cr (III)$(Ala)_2(Py)_2$]

Mixed ligand complexes of Zn(II) with anthranilic acid and slicylic acid have been synthesized by Md. Kudrat-E-Zahan and *et al.* [23]. Antimicrobial activity of the prepared complexes were measured as resistance to antimicrobial agents is emerging in a wide variety of nosocomial and community-acquired pathogens.

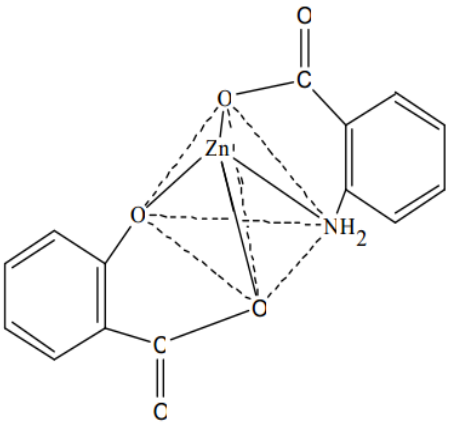

Fig 4: Structure of Complex [Zn (NH_2. C_6H_4. COO) ($C_7H_4O_3$)]

The Cd(II) Ni(II) Co(II) and Zr(IV) metal complexes containing a novel ligand naming bis(indoline-2-one)diethylenetriamine have been synthesized by Md. Kudrat-E-Zahan and et al. [24]. Antimicrobial activity of the prepared complexes was measured as resistance to antimicrobial agents is emerging in a wide variety of nosocomial and community-acquired pathogens. Cadmium complex is proven to have a higher antibacterial activity than the other metal complexes.

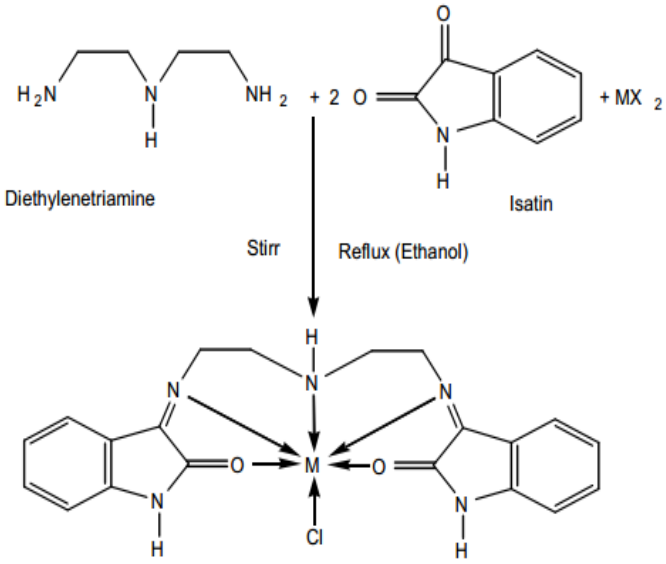

Fig 5: Synthesis of Cd(II) Schiff base complex. Where, M = Cd(II), Pd(II), Hg(II) and Zr(IV)

Md. Kudrat-E-Zahan and *et al.* [25] were synthesized Cd(II), Pd(II), Hg(II) and Zr(IV) complexes of bis(indoline-2-one) triethyelenetetramine which was made from isatin and triethylenetetramine. The ligand and the metal complexes were screened against various pathogenic bacterial species. The antimicrobial results indicate that the cadmium complex exhibit more activity than the palladium (II), mercury and zirconium (II) complexes. Transition metal complexes of Cu (II), Ni(II), Co(II) and Fe(III) Containing Bidentate Schiff

base, derived from the condensation of salicyladehyde and 2-aminophenol were synthesized and characterized by Md. Akter Farooque and *et al*. [26]. Mixed Ligand complexes of Ni(II) with amino acids and heterocyclic amines (fig.6) have been has been produced by Md. Kudrat-E-Zahan and *et al*. [27]. Antibacterial activity of the complexes has been examined against six (gram positive and gram negative) pathogenic bacteria by disc diffusion method and compared with that of standard antibiotic (Kanamycin). The complexes have been found to have moderate to strong antibacterial activity against the tested bacteria.

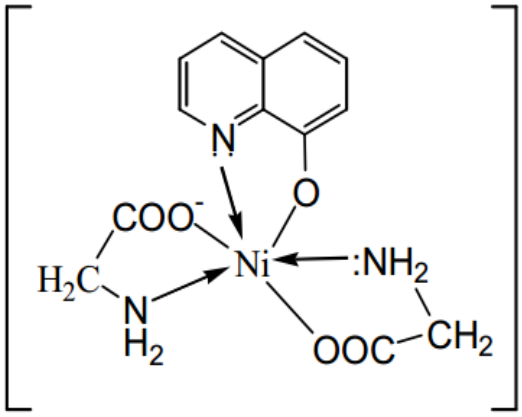

Fig 6: Structure of the complex [Ni(II)(Gly)$_2$(8-HQ)]

Md. Kudrat-E-Zahan and *et al.*[28] were synthesized Ag(I), Cr(III), Fe(III) and Sb(III) complexes of bis(indoline-2-one) triethyelenetetramine which was made from isatin and triethylenetetramine. The ligand and metal complexes were screened for antibacterial activity aganist various bacterial species. Copper(II) complexes containing two Schiff base ligands derived from 2-hydroxybenzaldehyde with 2-aminophenol and 3- aminophenol have been synthesized and characterized by Md. Kudrat-E-Zahan and *et al* [29] Bacteria, fungus, Entamoeba histolytica, and antineoplastic activities of the synthesized complexes have been determined by monitoring the parameters cell growth inhibition, survival time of tumour mice, time-body relation, causing of intraperitoneal cells and macrophages, alkaline phosphatase activity, hematological effect, and biopsy of tumour. Md. Kudrat-E-Zahan and *et al.* [30] were synthesized four new metal complexes of Co (III) with glutamic acid and heterocyclic amines. The antibacterial activity of metal complexes were tested against various bacterial species. The complexes showed strong to mode-rate activity against both the gram positive and gram negative bacteria indicating the higher zone of inhibition. Four new mixed ligand complexes of Ni(II) containing amino acids and heterocyclic amines have been prepared and characterized by Md. Kudrat-E-Zahan and *et al.* [31]. The antibacterial activity of ligand and metal complexes have been tested against various bacterial species. Transition metal complexes of Co(II), Cu(II), Ni(II) and Zn(II) Containing Bidentate Schiff base, derived from the condensation of ethylenediamine and 4-anisaldehyde have been prepared and characterized by IR, UV-Vis., and some physical measurements. IR spectral studies show the binding sites of the Schiff base ligand with the metal ion. Molar conductance data and magnetic susceptibility measurements give evidence for monomeric and electrolytic nature of the complexes. Structural studies show that all the complexes are tetrahedral. The mixed ligand complexes of Fe (III) with tartaric acid/succinic acid and heterocyclic amines have been synthesized and charaxterized by Md. Kudrat-E-Zahan and *et al.* [32]. New mixed ligand peroxo complexes of U(VI) and Mo(VI) with amino acids and heterocyclic amines have been synthesized and characterized by M. Saidul Islam and *et al.* [33]. Cytotoxic activities of the complexes have been examined against brine shrimp nauplii. U(VI) complexes were found to be more toxic to brine shrimp than Mo(VI) complexes. Transition metal complexes of Co(II), Cu(II), Ni(II) and Zn(II) Containing Bidentate Schiff base, derived from the condensation of ethylenediamine/o-aminophenol and cinnamaldehyde were synthesized and characterized by Md. Kudrat-E-Zahan and *et al.* [34]. The complexes have been found to have moderate antimicrobial activity against the tested bacteria. Mixed ligand complexes of Cobalt(II) with phthalic acid and heterocyclic amines have been prepared and characterized by M. Saidul Islam and *et al.* [35]. Antibacterial activity of the complexes were tested against various bacteraial species. Mixed ligand complexes of Co(II), Ni(II) and Cu(II) containing Phthalimide and heterocyclic amines have been synthesized and characterized by Md. Kudrat-E-Zahan and *et al.* [37]. transition metal complexes of Mn(II), Fe(III) Co(II), Ni(II), Cu(II), and Sb(III) containing the bidentate Schiff base derived from condensation of S-methyldithiocarbazate and cinnamaldehyde were synthesized by Md. Kudrat-E-Zahan [38]. The metal complexes have been screened against various pathogenic bacterial species. A novel bidentate Schiff base containing NS donor sequences was synthesized by condensing Smethyldithiocarbazate (SMDTC) with p-anisaldehyde. A series of complexes of the ligand with Cu(II), Ni(II), Zn(II), Pb(II), Co(II), Mn(II) and U(VI) were studied and characterized by various physico-chemical methods. Antimicrobial activity of the prepared complexes was tested as resistance to antimicrobial agents in a wide variety of nosocomial and community-acquired pathogens. The highest antimicrobial activity was detected for the complex of Co(II) against candida species.

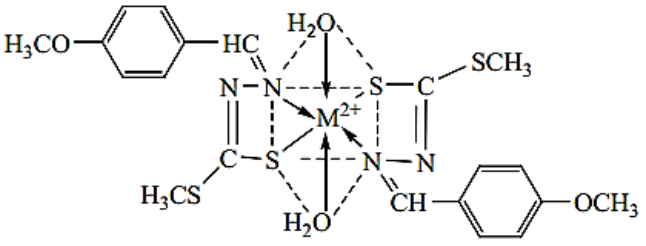

Fig 7: Octahedral structure of metal complexes containig SBDTC derived ligand.

A series of transition metal complexes of Cu(II), Ni(III) Zn(II), Cd(II), Co(II), Sb(III) and Fe(III) Containing Bidentate Schiff base, [N^I-(4-chloro-benzylidene)-hydrazecarbodithioicacid methyl ester] derived from the condensation of S-methyldithiocarbazate and P-chlorobenzaldehyde were synthesized and characterized by Abdul Alim and *et al.* [40]. Transition metal complexes of Co(II), Cu(II) and Mn(II) Containing Bidentate Schiff base, derived from the condensation of ethylenediamine and

Cinnamaldehyde were synthesized and characterized by Md. Kudrat-E-Zahan and *et al.* [41]. Binuclear Cr(III) metal ion complex was synthesized using diphenylacetic acid as primary ligand and 2-methyl pyridine (2-picoline) as secondary ligand. The synthesized compounds were tested against various pathogenic bacterial species. The complex showed moderate antibacterial activity with no antifungal activity [42]. Mixed-ligand complexes of Ni(II) and Zn(II) with Diphenylacetic acid and heterocyclic amines bases have been synthesized by Mst. Tasmina Khatun and *et al.* [43]. The synthesized complexes were tested against various pathogenic bacterial species. Metal complexes of Cr(III) and Sn(II) containing Schiff base ligand [4-{(pyridin-2-ylimino)methyl}phenol] derived from condensation of 2-amino pyridine with 4-hydroxybenzaldehyde was prepared by Md. Saddam Hossain and *et al.* [44]. The synthesized schiff base and their metal complexes have been screened for antibacterial activity against various pathogenic bacterial species. The Schiff base and its metal complexes have been found to have moderate to strong antibacterial activity. Mn(II), Fe(II), Co(II) and Sn(II) ions with tridentate N,O containing Schiff base ligand 2-{(4-hydroxybenzylidene) amino} phenol derived from condensation of 2-amino phenol with 4-Hydroxy Benzaldehyde have been prepared and characterized by Md. Kudrat-E-Zahan and *et al.* [45]. The ligand and metal complexes were tested against various gram positive and gram negative bacterial species. Mn(II), Fe(II), Co(II) and Cd(II) complexes with Schiff base ligand 4-{(pyridin-2-ylimino)methyl}phenol derived from condensation of 2-amino pyridine with 4-hydroxybenzaldehyde was prepared. The ligand and metal complexes were tested against various pathogenic bacterial species [46]. Laila Arjuman Banu and *et al.* [47] were synthesized Co(II), Cu(II) and Ni(II) complexes containing Schiff bases and Heterocyclic amines.The synthesis metal complexes were tested against various pathogenic bacterial species. Md. Saddam Hossain and *et al.* [48] Metal complexes of Cr(III), Co(II) and Cd(II) ions were synthesized with a ONS containing Schiff base ligand, 2-bis(2-oxoindolin-3-ylidene)hydrazinecarbothioamide which was derived from the condensation reaction of thiosemicarbazide and isatin. The ligand and complexes were isolated from the reaction in the solid form and characterized by IR, UV-Visible, Thermal analysis and some physical measurements. Spectroscopic evidence indicated that the Schiff base behaved as ONS coordinating hexadentate chelating agent. Magnetic susceptibility data coupled with electronic spectra suggested a distorted octahedral structure of the complexes. The synthesized ligand and metal complexes were tested for antibacterial activitiy study against various pathogenic bacterial species. Jasmin Ara Shampa and *et al.* [50] were synthesized Schiff base ligand and its Cu (II) complex by the condensation reaction of isatin with amino acids (cysteine / glycine / leucine / alanine). The Schiff base Cu (II) complex was subjected to antimicrobial studies screened by employing the Disc Diffusion method. All the synthesized complexes showed strong antibacterial activity. Metal complexes of Cu(II) and Co(II) ions with two Schiff base ligands {2-((2-hydroxybenzylidene) amino) phenol}and {2,2'-((1,2-phenylenebis (azanylylidene)) bis (methanylylidene)) diphenol} was derived from the condensation reaction of salicylaldehyde with 2-aminophenol and o-phenyldiamine respectively. The Schiff base ligands and their complexes were subjected to antimicrobial studies screened by using the Disc Diffusion method. All the synthesized compounds showed moderate to strong antibacterial activity. The complexes showed more antibacterial activity than their corresponding ligands [51]. Mst. Sadia Afrin Dalia and et al. [52] were synthesized Zn(II), Mn(II) and Ni(II) ions with tetradentate N, O coordinating Schiff base ligand [2-bis(2-hydroxybenzylidene)}hydrazinecarboxamide], ($C_{15}H_{13}N_3O_3$) were synthesized. The Schiff base ligand was derived from the condensation of semicarbazide hydrochloride and salicylaldehyde. Farhana Afsan and et al. [53] were synthesized Zn(II), Ni(II) and Mn(II) complexes containing Schiff base ligand derived from thiosemicarbazide and salicyaldehyde. Co(II) complexes containing Schiff bases derived from 4-hydroxy benzaldehyde and 4-amino benzoic acid also prepared and characterized. All the synthesized ligands and metal complexes were tested against various bacterial species. Three new Mo(VI) peroxo complexes [MoO(O2)(Val)2(IQ)2], [MoO(O2)(Val)2(2-Apy)] and K[$MoO(O_2)(Val)_2$(8-HQ)], where Val = Valine, 2-Apy = 2-Aminopyridine, IQ = Isoquinoline, and 8-HQ= 8-Hydroxyquinoline were reported by F. K. Camellia and *et al.* [54]. Four complexes of Cu(II) ions containing Schiff base ligands, $L^1(C_{20}H_{14}O_4N_4)$ [N,N`-Bis-(2-nitro-benzylidene)-benzene-1,2-diamine] derived from condensation reaction of o-phenylenediamine and 2-nitrobenzaldehyde, $L^2(C_8H_8N_3SCl)$[2-(2-chlorobenzylidene) hydrazinecarbothioamide] derived from condensation reaction of thiosemicarbazide and ochlorobenzaldehyde and $L^3(C_9H_{11}N_3OS)$ [2-(4-methoxybenzylidene)-hydrazinecarbothioamide, derived from the condensation reaction of anisaldehyde and thiosemicarbazide respectively by Kismat Ara Elachi and *et al.* [55]. All the ligands and complexes were tested for antibacterial activity against various bacterial species. Metal complex [Co (SB) (SCN)] (where, SB = 2-[(6-Amino-hexylimino)-methyl] phenol) have been reported by Md. Kudrat-E-Zahan and *et al* [56]. Several biomedical toxicological properties of the complex has been determined by monitoring the parameters cell growth inhibition, survival time of tumour mice, time body relation, causing of intraperitoneal cells and macrophages, alkaline phosphatase activity, haematological effect and biopsy of tumour. The synthesized Schiff base Co(II) complex was found to have anticancer and cytotoxic function. Ni(II), Cu(II), and Zn(II) complexes with Schiff base containing the nitrogen−sulfur donor chain [$(CH_3)_2N$–C_6H_4–CH=N–NH–C(S)–$SCH_2C_6H_5$] was prepared by the condensation of 4-(dimethylamino)benzaldehyde and S-benzyldithiocarbazate was reported by Md. Abdul Latif and *et al.*[57]. The biological activity testing results showed that the complexes were more potent antibiotics than the free ligand. The Cu(II) and Ni(II) complexes displayed high antibacterial potency and Zn(II) was moderately active against bacteria. A series of Schiff base complexes of U(VI) and Zr(IV) containing heterocyclic amines has prepared and reported by Laila Arjuman Banu and et al. [58]. The complexes have been found to have moderate to strong antimicrobial, antifungal and cytotoxic activity. Mixed ligand complexes of Ni(II) and Cd(II) with phthalic

acid/succinic acid and heterocyclic amines have been synthesized and reported by Jeasmin Akter and *et al.* [59]. The synthesized metal complexes were tested in various pathogenic bacterial species. Two new mixed ligand complexes of transiton metals were synthesized from a Schiff base (L^1) obtained by the condensaton reacton of isoniazid and p- anisaldehyde as primary ligand and 2.2′-bipyridine (L^2) as secondary ligand. The biological actvites of the new compounds were tested against Escherichia coli (*E. coli*) and Bacillus cereus (*B. cereus*) showing the enhance actvity of complexes against the species as compared to the free ligand [60]. Two complexes of Cu(II) and Ni(II) with the ligand N- (4-methoxybenzylidene) isonicotinohydrazide, having the formula $[M(La)_2]^{2+}$ (M = Cu(II) and Ni(II)) were synthesized. The ligand was synthesized by the condensation of isonicotinic acid hydrazide (isoniazid) with 4-methoxybenzaldehyde (panisaldehyde). In vitro antibacterial activity against human pathogens like gram negative Escherichia coli (*E. coli*) and gram positive Bacillus cereus (*B. cereus*) strains [61]. Ranjan K. Mohapatra and *et al.* [62] have studied the recent advancement of urea and thiourea based metal complexes.

Conclusions

In this work, the biological activity such as antibaceterial, anftifungal, cytotoxicity and anticancer effects of a some metal complexes containing schiff bases and various of coordinating ligands have been reviewed. The application of bioinorganic chemistry to medicine is a rapidly developing field. Novel therapeutic and diagnostic metal complexes are now having an impact on medical practice. Advances in bioinorganic chemistry are important for improving the design of compounds to reduce toxic side-effects and understand their mechanisms of action. This review reveals that the pharmacologically interesting metals could be a suitable strategy to develop novel therapeutic tools for the development of metal based drugs.

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